

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 February 2003 (06.02.2003)

PCT

(10) International Publication Number
WO 03/009827 A1

- (51) International Patent Classification: **A61K 9/00**
- (21) International Application Number: **PCT/US02/23184**
- (22) International Filing Date: **23 July 2002 (23.07.2002)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
60/307,710 **25 July 2001 (25.07.2001)** **US**
- (71) Applicant (for all designated States except US): **MI-CROBAN PRODUCTS COMPANY [US/US]; Suite 110, 11515 Vanstory Drive, Huntersville, NC 28078 (US).**
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **HANRAHAN, William, D. [US/US]; 9138 Whittel Place, Charlotte, NC 28216 (US). ONG, Ivan, W. [SG/US]; 5425 Cedworth Drive, Charlotte, NC 28210 (US). PARIANO, Laurie, J. [US/US]; 1615 foxtrot Drive, Charlotte, NC 28269 (US).**
- (74) Agents: **DOUGHERTY, Ralph, H. et al.; Dougherty & Clements & HOFER, Suite 400, 6230 Fairview Road, Charlotte, NC 28210 (US).**
- (81) Designated States (national): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.**
- (84) Designated States (regional): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).**

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/009827 A1

(54) Title: **ANTIMICROBIAL MELAMINE RESIN AND PRODUCTS MADE THEREFROM**

(57) Abstract: The present invention relates to melamine resins having incorporated therein one or more antimicrobial agents capable of providing permanent antimicrobial properties to the resin. The melamine resin is compounded with the antimicrobial as a finely divided powder diluted in a liquid forming a dispersion. The compounded melamine resin is useful for making melamine based decorative laminates used in flooring, countertops, dinnerware and other applications wherein a tough, mar resistant surface having bactericidal properties is required.

ANTIMICROBIAL MELAMINE RESIN AND PRODUCTS MADE THEREFROM

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims benefit under 35 U.S.C. section 119 of provisional application 60/307,710 filed July 25, 2001. The disclosure of this application is incorporated by reference herein in its entirety.

BACKGROUND OF THE INVENTION

1) Field of the Invention

The present invention concerns an antimicrobial melamine resin useful in making surface coatings and decorative laminates particularly for countertops, flooring, tabletops, desktops, and molded products such as molded dinnerware, picnic dishes, and cups, as well as surface treatments for textile and paper. More particularly, the present invention concerns the addition to melamine resin of an antimicrobial agent, which is capable of quickly and uniformly dispersing within the resin and exhibits antimicrobial properties for the life of the melamine layer.

2) Prior Art

Melamine resins are well known and were first synthesized in 1834 by Liebig. Prior to about 1940, these resins were more a laboratory curiosity than a commercial product. Today, melamine resin is widely used for surface coatings and decorative laminates. Paper based laminates are sold under the trade names of Formica® and Micarta®. These types of coatings or decorative laminates are formed from photographic prints or decorative

sculptured paper impregnated with melamine resin and placed on a core material and cured in a large press. The kraft paper impregnated with the melamine resin is very compatible with the melamine resin and costs less than multiple layers of impregnated paper.

Melamine resins have the hardest surface of any commercial material. This hard surface along with excellent grease and water resistance, low flammability, and clarity of the plastic has led to the usefulness of melamine formaldehyde as countertop material. These countertop materials are thin sheets composed of heavy paper or thin cardboard backing that is bonded to the backside of a patterned paper. The bonding material is usually phenolic, which may be foamed, but is not thick. The top layer of paper is impregnated with melamine formaldehyde. The laminate is heated and subjected to pressure to attain a complete cure. The material generally is between two to four millimeters thick, up to about two meters in width, and sold as a roll in lengths. The roll sheet is then adhesively bonded to a wooden base to make countertop, flooring, furniture, etc.

The melamine resin is compatible with a wide variety of fillers and has been used for many molded parts because of the hard surface that results. Many products such as molded dinnerware, plastic dishes, and cups are made from the melamine resin which is hard, stain-resistant, and relatively low cost.

Prego® flooring is a ready to use (no sanding and no urethaning) laminated flooring system having a top layer of melamine formaldehyde that is heated under pressure to fuse to a wood layer. The top layer is a wear layer that is space age tough and yet transparent so that it allows the wood grain to show through.

Although melamine resin, and its uses such as with Formica® or dinnerware, etc., are well known to those skilled in the art, making melamine resin having antimicrobial properties is quite difficult.

Despite the difficulty, there is a need in the industry to create tabletops, countertops, dinnerware, and flooring, all of which could be used either in a residential or commercial setting. More specifically, a restaurant having Formica® tabletops, countertops in the

kitchen, and flooring throughout the restaurant, all of which exhibit antimicrobial properties, would be desirable and would reduce the chances of contamination from salmonella, E. coli, and other bacteria and fungi. Melamine resins are very hard, producing surfaces from melamine resins that have permanent antimicrobial characteristics, as opposed to a topical treatment that only has a temporary and very short-lived duration, has heretofore been unknown. Additionally, certain classes of antimicrobial agents are compatible or react with the melamine such that they are incorporated into the resin and no longer exhibit antimicrobial properties.

Peroxide has been identified as an antifungal and mildew proofing agent suitable for melamine resins in Japan publication JP 10-119221 filed October 16, 1996 by Yozo Shioda. The peroxide is added at a concentration of 0.1 to 0.8 parts per 100 parts melamine. A problem associated with peroxide is that it rapidly degrades when heated, therein having shortened sustained antimicrobial properties. Additionally, at higher concentrations, the peroxide shortens the bath life of the melamine.

Antibacterial phosphates in combination with silver, benzalkonium, cety pyridinium and isopropylmethylphenol has been described for use with melamine resins in Japan publication JP 07-329265 filed June 3, 1994 by Kazuaki Tajima et al. for use in decorative laminates. The antibacterial phosphate along with silver, benzalkonium, cety pyridinium and isopropylmethylphenol is added to the overlay sheet or the printed sheet, and to the underlying kraft paper which is impregnated with phenolic resins. The phosphates require a secondary antimicrobial, in part because phosphates are a food source for a number of elemental plants and animals (bacteria and fungi). An antimicrobial system that does not employ phosphates would be preferred, and especially an antimicrobial system that does not provide a source of nutrition for the bacteria or fungi. Furthermore, a preferred system would be one in which the antimicrobial is concentrated in the overlay sheet.

The need for dinnerware, picnic plates, cups, etc. also having antimicrobial properties exists for basically the same reasons given above with respect to surface countertops, tabletops and flooring. To create a melamine based resin having permanent antimicrobial properties such that the antimicrobial agent is capable of migrating through

the very hard tough melamine resin, or is incorporated into the resin in such a manner that as the hard surface is abraded through normal wear and tear, newly exposed antimicrobial agent continuously renews the antimicrobial properties.

SUMMARY OF THE INVENTION

The present invention relates to melamine resins having incorporated therein one or more antimicrobial agents capable of providing permanent antimicrobial properties to the resin.

In the broadest sense, the present invention relates to the combination of a permanent antimicrobial melamine resin comprising melamine and an antimicrobial agent that is substantially inert with respect to the melamine resin and is present within the melamine resin in an amount effective to provide antimicrobial properties.

Effective antimicrobial agents are preferably those that have a relatively low vapor pressure. Triclosan, which is a diphenyl ether (bis-phenyl) derivative, having the scientific name of 2,4,4'-trichloro-2'-hydroxydiphenyl ether, is a particularly efficacious agent. It has a vapor pressure of 4×10^{-4} mm at 20° C. On the other hand, ortho phenyl phenol, (a.k.a. OPP - CAS No. 90-43-7), which has a boiling point of ~280 °C is generally considered too volatile in the instant invention, except in applications necessitating superior resistance to bio-fouling. The combination of OPP and triclosan have been found to exhibit synergistic effects, and in products having a melamine formaldehyde coating where anti-bio fouling properties is required, the use of OPP can be justified. Other antimicrobials agents include diiodomethyl p-tolylsulfone, zinc and sodium pyrithiones, azoles such as propiconazoles, poly(hexamethylene biguanide) hydrochloride, 3,4,4'-trichlorocarbanilide, barium metaborate-(H₂O)_n and silver, copper and zinc in zeolite or amorphous glass powder. In the invention, the antimicrobial(s) are delivered as a fine divided powder diluted in a liquid forming a dispersion. The dispersion is admixed with the melamine formaldehyde resins prior to the application of the resins. The dispersion is 15% to 65% solids by weight, and commonly 50% by weight, of the active antimicrobial. Zinc oxide can be added to the dispersion to stabilize the antimicrobial, and in particular zinc pyrithiones. The weight percent addition of the antimicrobial is 0.1 to 5%, with a preferred range of 0.3 to 1.0% on

the weight of the melamine resin.

In a typical application, such as forming a melamine formaldehyde based decorative laminate (i.e. flooring or countertop) the laminate is comprised of a high density core which is at least one layer of fiberboard, to which is adhered a melamine-formaldehyde impregnated printed paper sheet, and onto which is adhered a melamine-formaldehyde impregnated overlay sheet. The impregnated printed paper is patterned to have the desired design, which in the instant case, is for counters or simulated wood. Commonly, the printed paper sheet and the overlay sheet are pre-impregnated with the melamine formaldehyde coating at least several days prior to forming the laminate. The fiberboard is usually impregnated with a phenolic or melamine resin. The pre-impregnation of the printed paper and the overlay enables the melamine formaldehyde sufficient time to thoroughly wet-out the substrate, which in turn drives out any remaining entrapped air. The melamine-formaldehyde is usually applied as a compounded resin/water or resin/water/solvent(s) saturate. Solvent(s) that are commonly used in melamine formaldehyde compositions are usually rather complex mixtures or more than one solvent, and include aromatics such as toluene, xylene and Solvesso 150® an aromatic blend by Exxon; alcohols such as butanol, isobutanol, methanol, ethanol, isopropanol; esters such as cellosolve acetate, ethyl acetate isopropyl acetate; ketones such as isophorone, methyl ethyl ketone, acetone; alcohol amines such as dimethyl ethanol amine, dimethyl isopropanol amine; and ethers such as butyl cellosolve. The use of solvents generally is reserved for impregnating difficult to saturate paper. Certain grades of kraft paper are either too dense, or too hydrophobic or a combination of the two to be saturated to a sufficient level of pick up to achieve the desired properties with a pure water borne system. More open porous paper sheets can be saturated with water/ latex systems, which generally have the advantage of a lower raw material cost.

Compounding additives, in addition to the antimicrobial, include surface active agents such as wetting agents, surfactants, de-aerants, and defoamers; anti-blocking agents, catalysts such as PTSA (para toluene sulfonic acid), MSA (methane sulfonic acid), oxalic acid, ammonium nitrate and ammonium chloride; fillers; pigments; dielectric modifiers; glossing agents; and dyes. Latent acid catalysts, such as those having a fugitive

counter ion, like ammonium nitrate and ammonium chloride, are preferred where the storage time will be lengthy. Generally speaking the strong acid catalysts are only used in melamine formaldehyde systems where the melamine is highly methylated, such as hexamethoxymethylmelamine. The antimicrobial dispersion can be used with melamine, and alkylated melamines such as methylated melamines, butylated melamines, isobutylated melamines, and melamines containing imino resins such as methylated imino resins, butylated imino resins, isobutylated imino resins; and urea resins such as methylated urea resins, butylated urea resins, isobutylated urea resins formaldehyde resins; benzoguanamine resins and glycoluril resins.

Following saturation the carrier (e.g. water and / or solvent) is dried off leaving the sheet saturated with the compounded melamine formaldehyde amine. It has been found that the antimicrobial only need be added to the overlay to impart antimicrobial properties to the laminate. While it is anticipated that migration into the printed paper layer occurs, antimicrobial, and in particular bactericidal performance remains efficacious at the 0.1 wt. % on melamine level. The laminate is formed by combining the overlay, the printed paper and the fiberboard in a heated press. Typical cure times are 15 seconds to several minutes at 127 °C to 290 °C. Pressures are on the order of 1000 psi to 5000 psi.

Antimicrobial agents can also be added directly to melamine formaldehyde resins, wherein the melamine formaldehyde resin is being used as a surface coating, on countertops, flooring, tabletops, etc., the antimicrobial agent of the present invention is incorporated into the bath through which the kraft paper passes, for example. When the melamine formaldehyde resin is employed to make molded articles such as dinnerware, cups, chopping blocks, etc., the antimicrobial agent is incorporated directly into the melamine molding resin.

Suitable antimicrobial agents for the present invention may be 2,4,4'-trichloro-2'-hydroxydiphenyl ether (also known as triclosan); 2-phenylphenol; poly(hexamethylene biguanide) hydrochloride, 3,4,4'-trichlorocarbaniide, barium monohydrate, zinc omadine (derivatives of pyrrithione), and zeolites containing copper, silver, and zinc and. Because several of these antimicrobial agents are capable of reacting with the melamine

formaldehyde resin, they must consequently first be blended such that they are virtually encapsulated in a carrier that is compatible with melamine formaldehyde. This carrier containing antimicrobial agent is added to the melamine formaldehyde either in the bath when making solid surface materials or within the resin itself when compressed.

The present invention also pertains to products made from melamine resin having the antimicrobial agent incorporated therein. In the broadest sense, the present invention relates to an article, such as dinnerware, cups, glasses, flooring, countertops, tabletops, and cutting boards, which exhibit permanent antimicrobial properties during the useful life of such articles.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Melamine ($C_3H_6N_6$) is a white crystalline solid. Combining it with formaldehyde results in the formation of a compound referred to as methylol derivative. With additional formaldehyde (CH_2O) the melamine reacts to form tri-, tetra-, penta-, and hexamethylol-melamine. While commercial melamine resins may be obtained without the use of catalyst, both heating and catalyst are used to speed polymerization and curing. The reaction of the melamine with the formaldehyde is a condensation reaction with water as a byproduct. The curing of melamine resins is quickened by the use of heat and acid catalyst, while the overall pH is still neutral or slightly alkaline. The addition of acid catalyst provides a source for protons, but the level of addition is generally kept lower than alkalinity produced by the amines. Additionally, the melamine formaldehyde resin may contain fillers, plasticizers, dielectric modifiers, pigments or dyes, and glossing agents. When the resin is molded, the temperature range is generally between 154-171°C and under pressure in a compression mold from 2000 to 5000 psi.

Decorative laminates are usually assembled with a core of several sheets of phenolic or melamine resin impregnated kraft paper. The core is surfaced with a melamine formaldehyde impregnated sheet, which is often printed with a decorative design. Finally, a thin melamine resin-impregnated overlay sheet is applied. The sheets are impregnated by being passed through a resin bath, and followed by controlled moisture drying.

The melamine formaldehyde containing the dispersion of antimicrobial agent is incorporated into the saturating bath through which the paper passes. The bath is re-circulated to keep the dispersion equally distributed. A typical melamine formaldehyde saturant will have a viscosity of 300 to 600 centipoise. The percent solids is 55% to 58%. The pH is 9.3 to 9.8. The bath is long enough such that there is a dwell time of approximately 1 minute. The overlay sheet is a 43 lb (70 gsm) to 50 lb (80 gsm) sheet (3000 sq ft ream), which is saturated with 64.5 lb (105 gsm) to 68 lb (110 gsm) of resin (dry). The weight percent addition of the antimicrobial is 0.1 to 5%, with a preferred range of 0.3 to 1.0 wt.% on the melamine resin. The target weight percent of dry triclosan on melamine is 0.75%. Following saturation, the sheet is partially dried removing most of the dilution water. A similar saturation process is used on the impregnated printed paper sheet. The overlay, the printed paper sheet and the high density core fiberboard are assembled and laminated in a press at pressures ranging from 1000 to 1500 psi, at temperatures ranging from 170 to 210°C with a preferred temperature of 190 °C. The resulting laminate is mar resistant to detergents, acids, alcohols, oils and greases, and has antimicrobial properties throughout its entire life.

In a variation on the above described first embodiment, a second high density core fiberboard is formed, which is impregnated with melamine resin, and assembled and laminated to the first embodiment.

In a variation on the above described second embodiment, a rubberized pad is assembled and laminated to the bottom of the second high density core fiberboard.

Generally during curing, formaldehyde is released from melamine formaldehyde resin. Formaldehyde itself is a good antibacterial agent. However, when the curing is completed, insufficient amounts of formaldehyde are released and with time the amount released is smaller and smaller such that it simply has no antimicrobial effect, particularly after about one year as a molded article or in a surface material. The present invention relates to the incorporation of an antimicrobial agent in the melamine formaldehyde resin such that it always has antimicrobial properties throughout its entire life. The incorporation

is effected through the addition of a dispersion of the antimicrobial agent to the melamine formaldehyde resin. The melamine resin is coated / saturated onto an overlay sheet used in a laminate. Following coating, dilution water and / or solvent is dried off, leaving the overlay impregnated with uncured melamine resin containing at least one antimicrobial. The overlay is combined with other sheets under heat and pressure, to form the laminate. The antimicrobial agent, which is concentrated in the overlay of the laminate imparts protective antimicrobial properties to the laminate for the life of the melamine coating.

WHAT IS CLAIMED IS:

1. A permanent antimicrobial melamine resin, comprising: melamine and at least one antimicrobial agent in a dispersion which is substantially inert with respect to the melamine resin and is present within the melamine resin in an amount effective to provide antimicrobial properties.
2. A decorative laminate that has antimicrobial properties throughout its entire life, comprising:
 - an overlay sheet impregnated with a melamine resin containing an antimicrobial agent in a dispersion;
 - a printed paper sheet impregnated with a melamine formaldehyde;
 - a high density core fiberboard impregnated with a phenolic or melamine resin.
3. The permanent antimicrobial melamine resin as claimed in claim 1, wherein said antimicrobial agent is a chemical selected from the group consisting of triclosan, ortho phenyl phenol, diiodomethyl *p*-tolylsulfone, zinc pyrithiones, sodium pyrithiones, azoles such as propiconazoles, poly(hexamethylene biguanide) hydrochloride, 3,4,4'-trichlorocarbanilide, barium monohydrate and silver, copper or zinc in zeolite or amorphous glass powder.
4. A decorative laminate that has antimicrobial properties as claimed in claim 2, wherein said antimicrobial agent is a chemical selected from the group consisting of triclosan, ortho phenyl phenol, diiodomethyl *p*-tolylsulfone, zinc pyrithiones, sodium pyrithiones, azoles such as propiconazoles, poly(hexamethylene biguanide) hydrochloride, 3,4,4'-trichlorocarbanilide, barium monohydrate and silver, copper or zinc in zeolite or amorphous glass powder.
5. The permanent antimicrobial melamine resin as claimed in claim 1, wherein said antimicrobial agent is preferably triclosan.

6. The permanent antimicrobial melamine resin as claimed in claim 2, wherein said antimicrobial agent is preferably triclosan.
7. The decorative laminate that has antimicrobial properties throughout its entire life, as claimed in claim 2 further comprising a second high density core fiberboard impregnated with a phenolic or melamine resin.
8. The decorative laminate that has antimicrobial properties throughout its entire life, as claimed in claim 2, wherein said laminate is cured in a press at pressures ranging from 1000 to 1500 psi, at temperatures ranging from 170 to 210°C with a preferred temperature of 190 °C.
9. The permanent antimicrobial melamine resin, according to claim 1, wherein the weight percent addition of the antimicrobial agent is 0.1 to 5% on the weight of the melamine resin, with a preferred range of 0.3 to 1.0%.
10. A decorative laminate that has antimicrobial properties, as claimed in claim 2, wherein the weight percent addition of the antimicrobial agent is 0.1 to 5% on the weight of the melamine resin, with a preferred range of 0.3 to 1.0%.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/23184

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A 61 K 9/00

US CL : 428/907; 442/123-125; 106/2,15.05,38.2; 424/400-405, 411.1-413.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/907; 442/123-125; 106/2,15.05,38.2; 424/400-405, 411.1-413.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
PALM

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,248,342 B1 (TROGOLO et al.) 19 June 2001, see entire document.	1-4 & 7-10
Y	US 6,071,542 A (TANIMOTO et al.) 06 June 2000, see entire document.	1-4 & 7-10
A	JP 06198607 A (MARUYAMA SANGYO KK) 19 July 1994, see entire document.	1-4 & 7-10

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

04 September 2002 (04.09.2002)

Date of mailing of the international search report

27 SEP 2002

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Terrell Morris

Telephone No. 703-308-0661